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FACSIMILE REQUEST AND COVER SHEET

TO: Pete Stevenson	OFFICE: OSC
FAX NUMBER: 303 312 6071 ~~6067~~	# OF PAGES (INCLUDING COVER) 5
FROM: A. Humphrey	DATE: 1/30/98

MESSAGE:

Attached is a few pages from a ~~pp~~ ERT/REAC XRF paper. The 3rd page covers our method of samp prep (More Rigorous Preparation Method). Typically we do not use a microwave and we do not usually grind, unless your toxicologist makes us! If you want all 27 pages, let me know.

Information for sending facsimile messages:

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Although Table 5 details the expected detection limits for FPXRF analyzer, it is more appropriate to determine the DL for a specific project. Such a DL reflects instrumental and other variables for the set of samples analyzed. Note also that the data in Tables 5 and 6 were obtained by analyzing the standard 12 times consecutively. The detection limits thus listed are "short-term" data. Actual site data yields slightly larger DLs, reflecting instrument performance over several days or weeks. Thus a soil "standard" is analyzed periodically during field analysis. Then the standard deviation for the repeat analyses is calculated and used to estimate the detection limit for the analytes of concern.

The choice of an appropriate sample for determining actual site DLs requires some trade-offs. The use of a site background sample yields several advantages, because such a sample matches well with site soils in general composition, particle size distribution, and moisture content. Typically, site background soils are successfully used to determine MDLs. However, obtaining a representative and clean background sample is difficult. Therefore, to standardize the MDL determination, a certified standard soil, NIST 2709, available from the NIST, is used to estimate the DL. Table 7 details the composition of this soil certified by NIST. Most elements of interest for hazardous waste sites are present at trace levels, making this a useful standard for DL studies. The NIST 2709 sample has been prepared at finer particle size than the 10-mesh size common for most site samples. Therefore, because of particle size effects it provides concentrations by FPXRF analysis approximately 20% less than expected. Several other soil standards, including NIST 2710 and 2711, may be used to determine the analytical accuracy and precision at concentrations close to the action levels appropriate for site investigations.

As described previously, the half-lives of several of the isotopes used in FPXRF are quite short, resulting in a significant loss of intensity for the analyzers over several years. Table 8 details the 60-second DL data for one FPXRF analyzer over three years. Data is presented for similar samples over the time frame discussed. NIST 2709 standard was not available at the beginning of the study. The unit was refurbished in May 1995 by the manufacturer and the Cd-109 source was replaced. The DLs for those elements analyzed using the Cd-109 source (bold values in Table 8) markedly deteriorate from August 1992 through October 1994. The June 1995 data show a major improvement in the DLs for elements excited by the Cd-109 source (Cr(HI) through Rb). Most DLs have returned to the 1992 levels. Note that the DLs for the Fe-55 sources elements do not improve. The Fe-55 source was not replaced. No significant differences are seen for the elements using the Am-241 source over the time frame, which is very small compared its half-life (433 years).

FPXRF Analysis of Reference Materials

Typically, the elements of interest depend on the environmental application in question. Once the target elements are defined, suitable reference materials are selected for calibrating the FPXRF analyzer (if empirical calibration is required), for determining FPXRF detection limits, and for determining accuracy and precision. Standard reference materials (from NIST and other sources) are used for some applications (eg. analysis of soils). Site-specific calibration standards (analyzed by laboratory methods) are required when certified materials are not available for the matrix in question. Depending on site action level requirements, FPXRF analysis may not be suitable for some elements because of high detection limits, unresolved spectral and matrix interferences, and other instrumental limitations.

Table 9 shows typical FPXRF results for NIST soil standards (numbers 2710 and 2711). The FPXRF analyzer utilized three radioisotopic sources, a HgI semiconductor detector, and a FP calibration. Results were based on the average of eight measurements with 60 seconds acquisition time per source. A number of elements were below the FPXRF MDL. Typically, FPXRF results agreed within 20% with certified values for elements with concentrations significantly above (more than 10 times) the MDL. Spectral interferences made some elemental analyses difficult. The high Fe content produced high background for Mn and Co, and Pb severely interfered with As determination. Additionally, Ba results were approximately 30% below certified values. The data in this table illustrates the usefulness and accuracy of FPXRF for analyzing soil contaminants and demonstrates the need to adjust measurement times to obtain MDLs compatible with hazardous waste site objectives.

SAMPLING

When analyzing hazardous materials by XRF techniques, sample preparation is relatively simple with few restrictions on sample type because the spectral features in XRF are functions only of the inner-shell atomic structure. X-ray intensities for all but the lowest atomic number (lightest) elements are unaffected whether or not the fluorescing element is in elemental or compound form. X-ray intensities are independent of the physical state of the element (22). However, matrix effects resulting from variations in concentrations of interfering elements are important, and most field portable XRF analyzers correct for these effects when the application is calibrated (refer to the *Calibration and Quantitation* section for details).

Regardless of the instrumentation employed, there are two methods of sample preparation to consider when analyzing hazardous materials by XRF, *in situ* and discrete sampling (7,23,24). Typically, both methods are employed on the basis of the number of analyses required, site/contaminant history, time allocated to conduct site activities, and proposed sampling design. *In situ* analysis provides much more flexibility with a field-portable XRF unit by allowing rapid collection of data for a large number of sample points, eliminating physical sampling and chain of custody considerations, and yielding real-time data for rapid decisions in the field. To analyze contaminated soils, the XRF instrument is taken to the sample location and the probe placed directly on the soil surface to measure heavy metal contamination.

In the case of discrete sampling, significantly more preparation is required. This limits the number of measurements in the time for site activities. The payback for this effort is that analytical accuracy and precision are generally improved for prepared samples compared to *in situ* measurements. Site data quality objectives (DQO) determine which sample preparation method is most appropriate (25,26). Precautionary measures should be taken when petroleum contaminates the site because direct contact with the sample breaches the probe window (typ-

and moisture to damage the detector. All quantum sharp objects, such as stones and debris present during from the sample surface, may rupture the probe window. Typical procedures for *in situ* and discrete sample measurements are outlined next.

In situ Measurements

In situ measurements are well suited to XRF analysis of metal contaminants in soil and should typically be performed in the following manner (Fig. 3):

1. Identify the sample location.
2. Remove all surface debris and sharp objects that may rupture the probe window. The analysis area may be homogenized by mixing with a trowel to a specific depth. Flatten the area prior to analysis.
3. Optional—Cover the sample (if necessary, depending on the type of site), with a single-thickness plastic bag or 6.5-micrometer (0.2-mil) X-ray film to avoid cross-contamination. This is optional for a site where there is little risk of gross surface contamination. In the case of light (low atomic number) elements, the plastic bag significantly interferes with the measurement. For instruments requiring empirical calibration, if a plastic bag is used for sample measurements, calibration must be performed with the same plastic over the probe. In the case of instruments using FP-based calibrations, only a thin layer of 0.2 mil Mylar of polypropylene should be used to avoid potential quantitation errors. Refer to the *Sampling Considerations* section for more details.
4. Measure each sample location as follows: two to three points in a 1-foot by 1-foot area (0.3 × 0.3 m) or five points in a 3-foot by 3-foot area (0.9 × 0.9 m). Single *in situ* measurements may be made at any one sample location. However, the XRF results may not be representative.
5. Measure each location with sufficient counting time for each excitation source utilized to produce results compatible with site DQO.
6. Record all measurements, and report the average for each location.
7. Collect a minimum of 10% of the samples for confirmatory analysis. Prepare and analyze the samples using the XRF sample cup method described below, and submit the XRF cups for laboratory confirmatory analysis.

The probe should be placed firmly on the ground to maximize contact with the surface. If the surface or subsurface samples are wet, mock *in situ* measurements are performed where the sample is homogenized, placed in a labeled container, and allowed to air dry. Then the sample is formed into a flat cake, and the probe is placed flush against the top of the cake during analysis.

It should be noted that *in situ* measurements exhibit a high degree of variability due to the natural heterogeneity of the sample. An *in situ* sample preparation process (for example, mixing the sample prior to analysis) greatly reduces the short-range variability by reducing heterogeneity.

Discrete sample analysis involves physically collecting a sample (minimum of four ounces) and some type of field preparation before XRF analysis. Three types of discrete sampling are typically utilized in the field: plastic bag and mock *in situ* methods with limited sample preparation, and the XRF sample cup method with more rigorous sample preparation procedures (Fig. 4). Selection of the appropriate sample preparation procedure depends on the DQO established for the site.

Less Rigorous Preparation Methods

Plastic Bag Method

1. Identify the sample location.
2. Remove all surface debris.
3. Physically collect the sample (minimum 4 ounces) in a plastic bag and mix. The actual sample volume collected depends on the amount of error acceptable. If the area is homogeneous, which is rarely the case with many hazardous materials, volume considerations are not as critical.
4. Remove organic debris, rocks, and other extraneous material.
5. Homogenize the sample.
6. Analyze the sample by placing the probe firmly on the sample bag and measure through the bag. If a plastic bag is used for sample measurements, then calibration must be performed with the same plastic over the probe.
7. Shake the bag, and repeat the above sequence for a total of three measurements, or select another measurement location for the sample. If there is excessive variability between readings, rehomogenize the sample, or use the more rigorous method of sample preparation described next (optional).
8. Record all measurements and report the average for each sample.
9. For confirmatory samples (minimum of 10%), place the sample in one or more XRF sample cups, and cover each with 0.2-mil Mylar or polypropylene. Reanalyze the sample cups, and record results. Submit the XRF sample cups for laboratory confirmation analysis.

Mock In Situ Method.

1. Identify the sample location.
2. Remove all surface debris.
3. Physically collect the sample (minimum 4 ounces) in a bowl or plastic bag and mix.
4. Remove organic debris, rocks, and other extraneous material.
5. Spread the sample on a flat surface, and thoroughly air dry the sample.
6. Homogenize the sample, and form it into a flat cake (minimum one-half thickness).
7. Optional: Cover the sample (if necessary, depending on the type of site) with a single-thickness plastic bag or 0.2-mil X-ray film to avoid cross-contamination. This is optional for a site where there is little risk

the measurement. For instruments requiring empirical calibration, if a plastic bag is used for sample measurements, calibration must be performed with the same plastic over the probe. In the case of instruments using FP-based calibrations, only a thin layer of 0.2-mil Mylar or polypropylene should be used.

8. Place the probe on the sample cake, and analyze with sufficient time for each excitation source utilized to produce results compatible with site DQO. Repeat the measurement for a total of two or three analyses at different locations on the sample cake.
9. Record all measurements, and report the average for each sample
10. For confirmatory samples (minimum of 10%), place the sample in one or more XRF sample cups, and cover each with 0.2-mil Mylar or polypropylene. Reanalyze the sample cups, and record results. Submit the XRF sample cups for laboratory confirmatory analysis.

More Rigorous Preparation Method (XRF Sample Cup).

1. Identify the sample location.
2. Remove all surface debris.
3. Physically collect the sample (minimum 4 ounces) in a bowl, and mix. Transfer to a glass jar for storage.
4. Remove organic debris, rocks, and other extraneous material.
5. Thoroughly dry the sample. Air drying or using a convection oven at approximately 100°C are acceptable methods of sample drying. Care should be taken to assure that the oven is not set significantly above 100°C to avoid sample splattering and loss of the more volatile elements. Use of a microwave oven for drying is acceptable as long as there are no volatile elements or pieces of metal in the sample.
6. Sieve the sample through a 10-mesh stainless steel sieve.
7. Optional—Grind the sample. This step is optional and not typically recommended. However, if grinding was employed to generate the calibration standards, then samples must also be prepared in the same fashion.
8. Homogenize the sample thoroughly.
9. Place the sample in an XRF sample cup, and cover with 0.2-mil Mylar or polypropylene. Tap the sample cup on a table top to pack the sample against the X-ray window film. Analyze the sample with sufficient time for each excitation source utilized to produce results compatible with site DQO.
10. If multiple analyses are taken to verify homogeneity, shake the cup, and tap it on a table top before each analysis. Use a consistent packing procedure for all samples. Analyze for a total of one to three readings.
11. Record all measurements, and report the average for each sample.
12. Optional—Prepare and analyze field duplicate XRF sample cups for 5–10% of the samples.

[illegible] a minimum of 10% of the prepared XRF sample cups for laboratory confirmatory analysis.

Sampling Considerations

Representative Samples. To accurately characterize site conditions, samples collected must be representative of the site or area under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentration of the contaminant(s) of concern at a given time and location. Analytical results from representative samples reflect the variation in contaminant and concentration range throughout a site. Parameters affecting representative sampling include: (1) geologic variability; (2) contaminant concentration variability; (3) collection and preparation variability, and (4) analytical variability. Attempts should be made to minimize these sources of variability. For additional information, refer to the U.S. EPA/ERT Representative Sampling Guidance (27).

Sample Moisture. If soils or sludges are measured, the sample moisture content affects the accuracy of the analysis. Sample dilution decreases the apparent concentration as the moisture level increases. This effect is most severe for analytes with low energy X-ray lines (less than 5 KeV) and is negligible for elements with higher energy X-ray lines, for example, Pb. To some extent, the dilution effect is counteracted by the reduced matrix absorption for the analyte X-ray lines when water replaces the higher atomic number (and, therefore, more absorbing) soil/sludge matrix. The direction and magnitude of the bias introduced by moisture, therefore, depends on the analyte X-ray line energy and the composition of the sample. The overall error is minor when the moisture content is small (5–20%), but it is a major source of error when the soil surface is saturated with water (28). Because the concentrations of all elements affect each other in FP-based quantitation, reductions in calculated concentrations for elements with low energy X-ray lines lead to low results for elements with higher energy lines because the interelement corrections based on the concentrations of elements with low energy lines are underestimated. Soil samples should be dried when moisture content is greater than 20%.

Sample Placement and Probe Geometry. Sample placement is a potential source of error because the X-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same source to sample distance for all measurements. When performing *in situ* measurements, the user should ensure that the probe surface is parallel to the sample surface, which must be flat. The goal is to place a flat compacted soil surface against the probe's sample presentation plane, achieving maximum surface to surface contact between the sample and probe. Variations in measurement geometry cause X-ray signal attenuation and, consequently, erroneous results.

Physical Matrix Effects. Physical matrix effects (due to sample morphology) result from variations in the physical character of the sample and include parameters, such as particle size, uniformity, heterogeneity, and surface condition (7). These parameters vary depending on the conditions at each site and must be monitored closely to determine if they bias

analyte exists as very fine particles within a matrix composed of much coarser material. If two separate aliquots of the sample are prepared so that the matrix particles in one are much larger than in the other, then the relative volume occupied by the particles with analyte is different in each aliquot. If measured *in situ*, a larger amount of the analyte is exposed to the source X-rays in the sample containing finer matrix particles. This results in a higher intensity reading for that sample and, consequently, an apparently higher measured concentration for that element. If the samples are packed in XRF sample cups, then the sample with larger sized matrix particles gives a higher reading because the finer contaminated particles are packed against the window film, exposing a larger area to X-rays.

When prepared samples are stored in XRF cups, settling effects also bias results. If the cups are stored window film side down, the finer particles settle against the window, and XRF results are biased high for the elements in those particles. Conversely, XRF results are biased high for elements in larger particles if the cups are stored window film side up. To minimize these effects, the cups should be shaken and tapped on a flat surface to pack the sample against the window film before XRF analysis.

Depth of X-Ray Penetration. The maximum depth of X-ray penetration with sealed radioisotope sources is approximately 2 mm in a soil matrix. An X-ray tube source yields greater depth of penetration, but then the limiting factor becomes the depth from which fluorescent X-rays escape to be detected. XRF analysis of soils is a surface analytical technique regardless of the X-ray source and instrumentation involved. Because of this, as little as 5 mm of clean material masks contaminated soil. For field portable XRF analysis, this means that more than 5 mm of soil is considered infinitely thick (the depth at which 99% of the analyte X-rays have been generated). *In situ* measurements are always infinitely thick. However, when analyzing soil in sample cups, the material must nearly fill the XRF sample cup (at least three-quarters full) to ensure that the sample is effectively infinitely thick.

In Situ **Measurements.** *In situ* analysis presents a unique situation for XRF measurements. Because there is minimal sample preparation for these measurements, they exhibit a high degree of variability because of the lack of homogeneity and wide range of particle sizes and moisture content in the sample. Data obtained from *in situ* measurements is best suited for site characterization activities for the objective of obtaining a quick overview of site conditions at the surface. Based on these initial measurements, a more rigorous sample preparation procedure may be required for additional analyses.

Effects of Sample Containers. The composition and thickness of materials located between the sample and probe window affect absorption of light element X-ray lines which, in turn, affect results from FP-based instruments (29). Measurements made with XRF sample cups should employ 0.2-mil Mylar or polypropylene X-ray film, which have negligible attenuation effects for most contaminant element X-ray lines and have uniform thickness and composition. If plastic bags are used to collect and measure samples, the XRF analyzer must be calibrated with the same thickness plastic to minimize these effects. In the case of instruments using FP-based calibrations, only a thin layer of 0.2 mil Mylar or polypropylene should be used to protect the probe from cross-contamination.

QA/QC AND DATA INTERPRETATION

Quality Assurance Objectives and XRF

For each data collection activity at a hazardous waste site, a quality assurance (QA) objective must be specified that corresponds to the ultimate data use objective. The U.S. EPA has defined three objectives (QA1, QA2, and QA3) for assessing and substantiating data collection (25). The characteristics of each QA objective should be evaluated to determine which one or combination fits the data use objective(s) for the site.

QA1 is a screening objective to afford a quick, preliminary assessment of site contamination and is suitable for data collection activities that involve rapid, nonrigorous methods of analysis and quality assurance. These methods are used to make quick, preliminary assessments of the types and levels of contaminants. QA1 is intended to facilitate collection of the greatest amount of data with the least expenditure of time and money. Data collected for this objective may be nonanalyte-specific and may not definitively identify contaminants or definitively quantitate their concentration.

QA2 is a verification objective to verify screened data (field or laboratory) or data generated by any method that satisfies the QA2 requirements. A minimum of 10% verification of results is required. This objective is suitable for data collection activities that require qualitative and/or quantitative verification of all or a select portion (10% or more) of the data. It is also appropriate for sample results acquired by nonrigorous methods of analysis and quality assurance. QA2 gives a level of confidence for a select portion of the preliminary data. It provides quick information on specific pollutants and concentration levels by using field-screening methods while verifying at least 10% of the data by more rigorous analytical methods (U.S. EPA-approved) and quality assurance. Results for the 10% of substantiated data give an associated sense of the quality for the results of the remaining 90%.

QA3 is a definitive objective for assessing the accuracy of the concentration level and the identity of the analyte of interest. It is suitable for data collection activities that require a high degree of qualitative and quantitative accuracy. Rigorous analytical methods and quality assurance are conducted to give a high level of confidence in the quantitative results for "critical samples." This facilitates decisions based on action levels for site remediation, health risk or environmental impact, cleanup verification, pollutant source identification, delineation of contaminants, and other significant factors. Only analyte-specific methods are used for the QA3 quality objective. Error determinations must be made for all analytes of interest for each critical sample.

XRF measurements fit into QA1 or QA2 objectives. If the site objectives are characterizing or determining the relative magnitude of contamination, XRF measurements fit the QA1 objective. If verification of the extent of contamination or verification of cleanup effectiveness is required, QA2 objectives are attained by submitting a minimum of 10% of the samples for confirmatory analysis by a U.S. EPA-approved laboratory method (such as atomic absorption [AA] or inductively coupled plasma [ICP] analysis). XRF is rarely used in conjunction with